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Deposit and Mobility of Cadmium in a Marsh-Cove Ecosystem and the Relation to Cadmium Concentration in Biota

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The study reported here presents the results of an investigation of a marsh-cove ecosystem heavily contaminated by cadmium. The most contaminated aquatic sediments were dredged in 1972-73, but the resuspension of the sediments and recycle of water from the dredge spoil resulted in reestablishment of a large contaminated sediment bed with concentrations very similar to those observed before dredging.

The stability of the sediment concentrations and shallow depth of the cadmium in the sediments indicate that the deposit is relatively stable in agreement with the expectations based on the water chemistry of the system.

Uptake does occur in both marsh and aquatic plants and all species of animals tested. Significantly elevated concentrations are observed compared to noncontaminated areas; however, edible portions of most fish do not appear to present a hazard. Crabs appear to present the most likely source of a hazard to humans. This potential hazard is still under investigation.

The dredging removed about 5.5 MT of cadmium, about one-fourth of that originally estimated to be present, but twice that amount is found to be in the cove sediments 3 to 4 years after dredging. No appreciable improvement in the ecosystem has been made, and more careful consideration should be given to the need for decontamination and the method of removal of contaminated aquatic sediments in any future case.

Introduction

The waste discharges of a nickel-cadmium battery plant during the late 1950's and through the 1960's produced highly contaminated sediments in Foundry Cove near Cold Spring, New York State (*1–3*). Very high cadmium concentrations were observed in an original evaluation by Gregor (unpublished results) and confirmed by studies in our laboratory and by the U. S. Environmental Protection Agency. Dredging of the major deposits in 1972 and the spring of 1973 upset the system; however, what appeared to be the original pattern of the deposits was re-established by the summer of 1973 (*3*).

Continuing studies have defined a generally stable distribution of the cadmium as re-established subsequent to the dredging. The cadmium, while relatively immobile, is available to the organisms in the system with all biota sampled showing contamination to some degree. The results do not indicate potential for a public health effect except through ingestion of contaminated crabs.

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Experimental

Analyses have been made by dissolution of acid-soluble materials followed by measurement by means of atomic absorption spectrophotometry with either flame or carbon-rod sources as dictated by sample size and metal concentrations. The sampling and analytical procedures used have been described in detail elsewhere (*1–3*) for the flame methods.

Analysis of NBS beef liver by the carbon-rod method used for tissue samples after dissolution with nitric, sulfuric, and perchloric acids (*4*) gave results of 0.26 ± 0.38 μg/g dry weight (10 samples) compared to NBS certified results of 0.27 ± 0.04 μg/g dry weight.

Results

Sediment Concentrations

The data shown in Figure 1 indicate that the dredging caused a significant shift in the 1971 1000 mg/kg cadmium contour. The area outlined by that contour was dredged to a 1-ft depth, but refilled with sediments and the new contour was established no later than the summer of 1974. Only minor changes have occurred in the period from July 1973 through 1975. The contours for higher concentrations in Figure 2 did not shift from 1974 to 1975.

Several profiles are shown in Figure 3 for core samples taken in 1976. Surface concentrations (0–5 cm) are not different from 1974-75 data for these locations, and the profiles indicate very little penetration of cadmium into the sediments. Cd/Ni ratios decrease with depth, as can be seen in the concentration profiles, and also decrease with distance from the original outfall. Similar observations have been reported and interpreted as indicating relatively greater mobility for nickel (*5*).

Water column concentrations have been shown to vary both with location and the stage of the tidal cycle (*2*). Values of as much as 65 to 90 μg/l. have been observed for dissolved cadmium, and 10 μg/l. is not unusual near highly contaminated sediments. Elevated concentrations are observed only on the ebb tide when disturbance of the sediments occurs at exposed sites. The results are highly variable

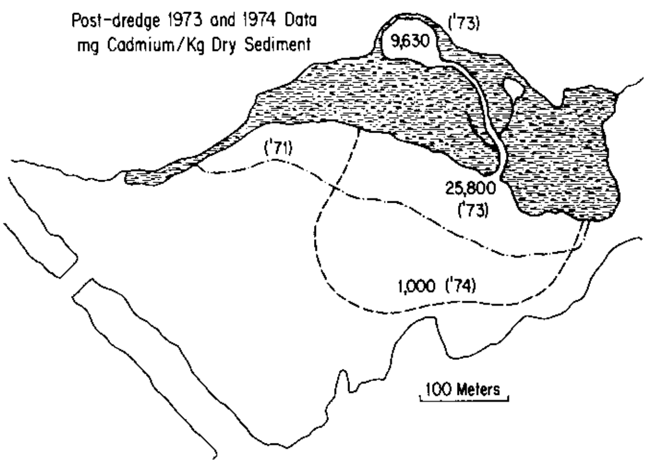

FIGURE 1. Changes in 1000 mg/kg contour. Pre-dredging contour at 1971 line as per Gregor (unpublished data): post-dredging contour 1974 line. The immediate area of the discharge at 9630 mg/kg is much lower than 1971 values, while the channel mouth is nearly unchanged from 1971.

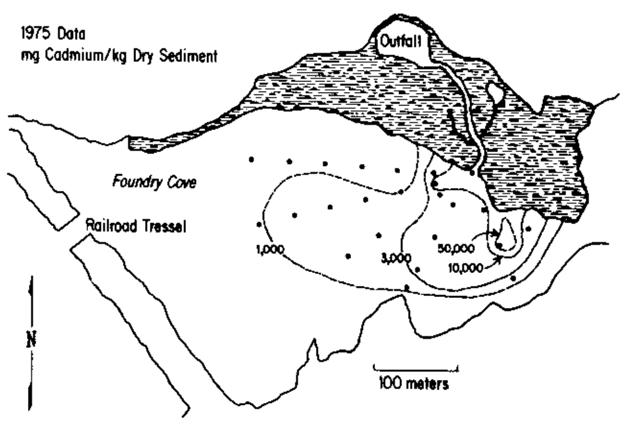

FIGURE 2. Estimated contours in 1975. Sampling points used are indicated as dots.

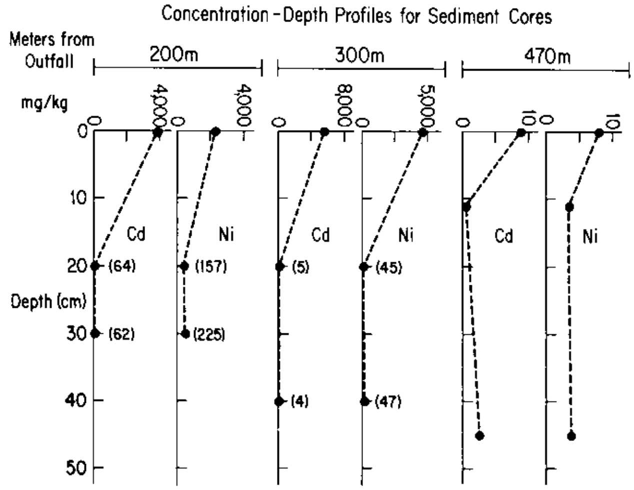

FIGURE 3. Concentration profiles in cove sediments at various distances from the original discharge point.

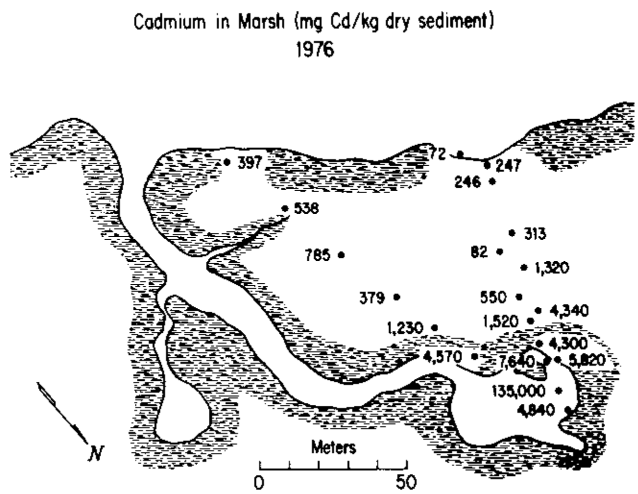

FIGURE 4. Concentration of cadmium in marsh sediments (mg/kg dry sediments) which are submerged only on high tide.

Table 1. Concentrations of several metals in bottom sediments, 1973.

Distance from outfall, m	Metal concn, mg/kg (dry) Fe[a]	Mn[a]	Co[b]	Zn
10	23,100	642	224	360
60	30,500	876	248	339
175	21,700	497	552	352
300	27,050	507	24	266
310				
360	—	—	—	—
400	20,700	401	12	—
420	—	—	—	—
480	18,000	516	<20	176
480	28,800	656	41	390
580	—	—	—	—
600	—	—	—	—
660	28,200	406	40	396
690	29,600	598	<52	1,140
710	22,800	—	18	350
720	—	—	—	—
760	52,300	545	27	—
860	—	—	—	—
880	—	—	—	—
900	21,000	443	19	358
1400	29,100	469	—	380
1530	28,100	475	—	510
1800	26,500	412	<15	467
2100	15,560	527	< 6	376
2330	26,850	636	<16	463
2510	18,265	824	<17	348
2530				

[a] Mean of 2-10 samples.
[b] Median.

from tide to tide and related to wind, tide, and river traffic among other possible sources of wave action. Nevertheless, the repeated tidal disturbances which cause transfer of both suspended solids and dissolved metals are no doubt a major factor in establishing the observed distribution and in determining the overall mobility of the metals.

Concentrations found in the marsh area are shown in Figure 4. These sediments, which are submerged at high tide only, also shown a pattern of decreasing cadmium concentration with distance from the outfall.

Data for Fe, Mn, Zn, and Co are given in Table 1. It is clear that of these elements only Co shows a concentration gradient related to the location of the outfall. This element was used as an additive in battery manufacturing at one time, and would have been present in the discharges (Zoch, personal communication).

Biota

The concentrations of cadmium found in several species of plants are given in Table 2. In every case it is clear that those species found in Foundry Cove have elevated cadmium concentrations compared to other locations.

The relation between cadmium concentrations in *Typha angustifolia* (leaves and rhizomes) and marsh sediments is shown in Table 3. The ratios of plant tissue to sediment concentrations incrase for both materials only where sediment concentrations fall below 1000–1500 μg Cd/g sediment. Data for the concentration of Cd in interstitial water in these locations are not available, but interstitial water values of approximately 10 μg Cd/l. have been reported (*6*) for both high (30,000 μg/g) and low (~ 1500 μg/g) sediment cadmium concentrations. The tissue cadmium concentrations are likely to be more closely related to interstitial water–cadmium concentrations (and chemical species) than to concentrations in sediments.

Concentrations observed in a variety of animals found in the cove are given in Table 4. Again, it is clear that cadmium, despite the relatively stable nature of the sedimentary deposits, is readily available for transfer to the biota. Most samples of edible fish flesh show values as low or lower than those for Stony Point samples (about 15 miles downstream) or not much higher than National Marine Fisheries samples. Eels, frogs, and crabs may be more elevated than finfish.

Table 2. Cadmium in plant species.

Location	Species	Cd, μg/g dry weight[a] EPA-1971	NYU-1973
Vanderburgh Cove (35 mi north)	*Typha* sp.	14	—
	Pentederia coradata	15	—
Cove (1 mi north, no name)	*Peltandra virginica*	28	—
Foundry Cove	*Peltandra virginica*		8.1-510
	Typha angustifolia	50-96	3.6-32.3
	Pentederia coradata	2-78	5.3 (same location) 269 (nearer source)
	Myriophyllum sp.	31-180	22-213

[a] Converted from wet weight by multiplying by 6.

Tissue burden patterns observed in laboratory uptake studies can be compared to those from field captured organisms as in Table 5 to determine the most likely manner by which field exposures are occurring. Species, exposure route, cadmium concentration, and length of exposure may all affect these patterns to some degree. However, it seems clear that ingestion must be a major route of exposure in the field. The higher level exposures in Table 5 (food 24 μg/g dry weight and water 250 μg/l.) produced total ingestion of 11.0 μg and exposure via water of 5.7 μg (calculated as flowing past the gills). Of these totals, 3.11 μg (28%) and 1.26 μg (22%) were found to be in the fish.

Table 3. Cadmium in *Typha angustifolia* compared to sediment cadmium concentrations.

Distance from outfall, m	Cd, ppm dry weight (mg/kg)			R plant/sediment
	Sediments	Leaves	Rhizomes	
32	5,820	47.6	—	8.2×10^{-3}
48	4,340	24.4	—	5.6×10^{-3}
63	1,320	26.2	—	20.0×10^{-3}
77	312	22.1	—	71.0×10^{-3}
96	246	1.5	—	6.1×10^{-3}
101	247	3.8	—	15.0×10^{-3}
—	150	—	240	1.6
—	320	—	250	0.8
—	330	—	1,400	4.4
—	850	—	550	0.6
—	15,000	—	3,000	0.2

Discussion

Water and Sediments

The water and sediment chemistry of this system are the most critical factors in determining both the distribution and effects of cadmium. The data in Table 6 show the system to be neutral and to contain significant amounts of carbonate. These water quality parameters are strongly dependent on the condition of the Hudson River which is the source of the tidal influx (3-4 ft depth difference from low to high tide). The sediments have produced a mixed $CaCO_3 \cdot CdCO_3$ compound where the concentration of cadmium is high, and at locations with lower concentrations, cadmium appeared bound to the organic fraction in the sediments (*6*). As might be pre-

Table 4. Cadmium in organisms from Foundry Cove as compared to other areas.

Organism	Cd, μg/g dry weight[a]						n
	Edible parts (muscle)	Liver	Kidney	Gills	Gut	Other	
Finfish[b]	<0.1–>0.4[c]	—	5–100	—	—	0.4–1.2	
Mollusca[b]	—	—	—	—	—	0.4–>12 (whole)	
Crustacea[b]	0.1–1.2	—	—	—	—	—	
Blue crabs[b]	0.8–1.2	—	—	—	—	—	
Eels (Foundry Cove)[d]	—	1.4	332	3	—	—	
Sunfish (Foundry Cove)[d]	1,10	—	—	—	—	—	
Plankton[d]							
Inside cove	—	—	—	—	—	40–890	
Outside cove	—	—	—	—	—	5–640	
Gammarus sp.[e]	59[f]	—	—	—	—		30
Fundulus diaphanus[e]	0.6	15.6	26.9	6.8	16.6		4
Fundulus diaphanus (Stoney Point)	1.8	4.2[g]	3.0[h]	2.3[i]	1.6[g]		9
Sunfish[e]	0.6	28.8	33.8	3.1	21.3		7
Eel[e]	3.8	121	103	10.3	27		1
Blue crab	0.4–32	26	—	24	25		4
Pickerel frog							
High Cd marsh[j]	12	267	640	—	800		1
Low Cd marsh[k]	4.2	13	37	—	62		1

[a] For wet weight basis divide by 4.
[b] Reported by National Marine Fisheries Service (*7*).
[c] Only one of 44 species exceeded 0.1.
[d] U. S. EPA, unpublished results from Foundry Cove, 1971.
[e] Foundry cove, 1976 samples (present study).
[f] Whole organism.
[g] Difference from Foundry Cove value significant at 99 LC.
[h] Difference from Foundry Cove value significant at 90% LC.
[i] Difference from Foundry Cove value significant at 95% LC.
[j] Caught May 14, 1976 over marsh where Cd concentration ranged between 1000 and 5000 μg/g.
[k] Caught August 31, 1976 over marsh where Cd concentration ranged between 70 and 300 μg/g.

Table 5. Comparison of tissue distribution in laboratory and field exposures.

	% of body burden		
	Gut[a]	Gills	n
Laboratory (*Carassius auratus*)			
Ingestion (food-24 $\mu g/g$ dry wt.)	60	21	4
Water (250 $\mu g/l.$)	22	52	4
Water (10 $\mu g/l.$) (*Fundulus diaphanus*)	23	29	9
Field (Foundry Cove)			
Captured (*Fundulus diaphanus*, sunfish	52	6	8
Implanted (*Carassius auratus*) (exposed in minnow trap for 5 days)	55	12	2

[a] Exclusive of contents.

Table 6. Range of water quality parameters at four stations within foundry cove and vicinity.

	1973[a]	1974[b]
Temperature, °C	6–27	4–28
Dissolved O_2, mg/l.	5–13	6–15
pH	7.0–7.6	7.1–7.4
Alkalinity, mg/l.	30–63	45–70
Total hardness, mg/l.		68–205
Chloride, mg/l.		25–600

[a] 14 samples at each of four stations, March–December.
[b] 8 samples, March-October.

dicted, the system appears to be at a steady state with cadmium relatively immobile in the surface layers of the sediment. This state has been restored subsequent to the dredging in 1972-73.

During the period of this study, fresh water flows in the river have kept chloride concentrations at low levels in the Foundry Cove region. During the 1960's, drought conditions resulted in elevated salinity in the region and proposals for use of the river as a major water resource could cause this to occur with or without recurrence of a major drought. We have found that mixing the sediments with an artificial seawater solution containing chloride at 15% of seawater salinity causes a significant release of cadmium.

Estimates of the total quantity of cadmium in sediments are very dependent on estimated depth profiles. The earliest estimate of the quantity of cadmium in the cove was 23 MT (Gregor, unpublished data) and a recent estimate of 18 MT was made by recalculations from the original data (*5*). About 5.5 MT was estimated to have been removed and buried by dredging (New York State, Department of Environmental Conservation, unpublished data); thus some 12 to 20 MT remains to be accounted for.

Using data available in court documents, EPA reports and memos, and a recent publication (*5*), in addition to our own studies, a table can be constructed to include estimates of cadmium found in given areas at various times (Table 7).

Table 7. Sediment cadmium contents.

	Sediment Cd, metric tons (MT)			
Area	1970-71	1973	1974	1975
Outer Cove	2[a]	—	2[b]	(2?)[b]
Inner Cove				
<1000 $\mu g/g$	—	0.2[c]	—	0.1[d]
>1000 $\mu g/g$	23[e]	—	9.0[d]	9.1[d]
Channel	—	—	2.4[d]	1.2[d]
Outfall area	(13)[f]			
Bird sanctuary channel	—	0.09[c]	—	0.04[d]
Total	25 (20)[g]	—	13.4	12.4

[a] By general agreement of EPA and NYU data with data of Bower et al. (*5*).
[b] Data of Bower et al. (*5*); 1975 estimate of 2 MT in the Outer Cove based on the assumption of continued stability from 1971-1974.
[c] From NYU data shortly after completion of dredging.
[d] NYU samplings for contour descriptions.
[e] Unpublished data of Gregor.
[f] Outfall estimate included in the Inner Cove estimate of 23 MT.
[g] The 20 MT estimate was calculated from unpublished data from several sources.

Quantities have been calculated from the average concentration in samples of the upper 5 cm with the assumption of a linear decrease to background at a 20 cm depth. When the 5.5 MT estimated to be in the dredge spoil is added to the 1974 and 1975 totals, values of 18.9 and 17.9 MT are obtained, in good agreement with the earlier estimates.

The data from 1975 show decreases in the cadmium found where sediments were originally rather lightly contaminated, while the heavily contaminated area of the cove remained essentially unchanged. These changes in the less contaminated areas present only a small overall change two years after the dredging of 1972-73. While the outfall area has had a major fraction of the deposited cadmium removed by the dredging, the larger area of the cove sediments which were dredged returned to the concentrations originally found and this area was relatively stable for at least two years after completion of the dredging.

Dissolution and transfer of the remaining 2 MT in the outer cove or the total of 11 MT in outer and inner coves to the river over a single tidal cycle (an unlikely event) would produce an estimated average concentration in one tidal volume (7.7×10^7 m^3) of 25 to 140 μg Cd/l. Dilution of net discharges measured on several days at 1.5 to 13 $\mu g/l.$ over a single tidal cycle at the trestle would result in 0.08 to 0.7 $\mu g/l.$ if dilution occurs in the drought fresh water flow of 55 m^3/sec, or 0.008–0.07 $\mu g/l.$ at normal fresh water flow rates. The likely event thus might be a release resulting in a concentration of up to 0.7

$\mu g/l.$ of river water. This is not unlike the values of 1 μg often found in natural waters (including the Hudson River) (*8*). Even the higher values of 25 to 140 $\mu g/l.$ would be reduced by tidal mixing and equilibration with suspended solids over a period of several days. However, in the latter case some toxic effects might well be observed (*9*).

Biota

The distributions found in the tissues of plants and animals show a significant availability of cadmium to the biota despite its relative stability in the sediments. Patterns of high liver concentrations in the organisms relative to the kidney concentrations indicate a considerable rate of continuing exposure. Further evaluations of the patterns of organ burdens and the possible relations to exposure are in progress and will be reported elsewhere.

Comparisons of organ burden distributions for field captured *Fundulus diaphanus* and implanted *Crassius auratus* to those for laboratory exposed fish show that the field specimens had ingestion as a major route of exposure.

We have reported (*3*) that the sediment areas with cadmium concentrations exceeding 1000 μg Cd/g sediment dry basis show some indication of decreased numbers of bethic organisms, and the effect is very significant where concentrations exceed 10,000 $\mu g/g$. The presence of an effect on ecosystem population numbers and diversity would obviously be a function of the fraction of the sediment area contaminated at an effect level. The total area at 10,000 μg Cd/g sediment is relatively small, and no effect would be expected on overall area populations of insects maturing from the benthic larval forms.

Population studies have failed to show clear cut effects on planktonic species (*9*); however, the laboratory studies indicate that *Daphnia sp.* may be affected in the system by the repeated concentrations of 10 $\mu g/l.$ Cd in solution. Some possibility exists for chronic effects on animals or other larger organisms present in the area (muskrats, turtles, etc.), but no population counts have been made, nor has data been obtained regarding fish population numbers.

Human Exposures

Exposures to local residents could only occur from ingestion of organisms caught in the area, as no recreational swimming occurs in the cove, and the water is not used for drinking purposes. Frog hunting is not known to produce significant catches, and commercial fishing for eels has been prohibited in the Hudson River because of the PCB contamination. As muscle tissue for other fish appears to be in the normal range for data reported by others (see Table 4), the blue crab appears to be the only likely source of a hazard.

The crab has been harvested in numbers at Foundry Cove by local residents over the period 1972-76. As some residents have reported eating as many as 300 crabs per year, there is a potential for ingestion of significant quantities of cadmium above the 57–71 μg/day tolerance value suggested by WHO (*10*), this exposure route is under continuing study.

Conclusions

The removal of the original deposits of cadmium from Foundry Cove was only partially successful. Redistribution of cadmium in solution and on fine suspended solids during and after the dredging has re-established a large area of contaminated sediments with a pattern very similar to that outlined by sampling performed prior to the removal.

Several years after the dredging the plants and animals in the cove continue to be contaminated despite the relative stability of the cadmium in the sediments. Organ burden patterns support the conclusion that exposures are both current and at significant rates.

The effects present in Foundry Cove do not seem sufficient to justify a further removal effort. Should the migrant crab population be found to be sufficiently contaminated to represent a hazard, a ban on crabbing in a relatively limited region should suffice to prevent excessive human exposures.

Prior to decisions regarding removal, the hazards of contaminated sediment beds must be carefully considered in terms of existing effects, the likelihood of redistribution during removal, potential long-term impact of the bed as is and/or if redistributed, and the costs of the best removal action.

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REFERENCES

1. Kneip, T. J., Ré, G., and Hernandez, T. Cadmium in an aquatic ecosystem: distribution and effects. In: Trace Substances in Environmental Health–VIII. 1974. A Symposium, D. D. Hemphill, Ed. University of Missouri, Columbia, Mo.,

1975.
2. Kneip, T. J., Hernandez, T., and Ré, G. Cadmium in an aquatic ecosystem: transport and distribution. In: Proceedings of the Second Annual NSF-RANN Trace Contaminants Conference, Asilomar, California, August 1974, pp. 279-283.
3. Kneip, T. J. Effects of cadmium in an aquatic environment. In: Edited Proceedings, First International Cadmium Conference, San Francisco, Metal Bulletin, Ltd. London, England, 1978, pp. 120-124.
4. Blood, E. R., and Grant, G. C. Determination of cadmium in fish tissue by flameless atomic absorption with a tantalum ribbon. Anal. Chem. 47: 1438 (1975).
5. Bower, P., et al. Heavy metals in the sediments of Foundry Cove, Cold Spring, New York. Environ. Sci. Technol. 12: 683 (1978).
6. Bondietti, F. H., et al. Proceedings of the First Annual NSF-RANN Trace Contaminants Conference, Oak Ridge, Tenn., Aug., 1973, CONF-730802, ORNL, Oak Ridge, Tenn., 1974, pp. 211-224.
7. National Marine Fisheries Service. First Interim Report on Microconstituent Resource Survey, Southeastern Utilization Research Center, College Park, Md., 1975.
8. Fleischer, M., et al. Environmental impact of cadmium: A review by the panel on hazardous trace substances. Environ. Health Perspect. 7: 253 (1974).
9. Fennikoh, K., Hirshfield, H. I., and Kneip, T. J. Cadmium toxicity in planktonic organisms of a freshwater web. Environ. Res. 15: 35 (1978).
10. Mahaffey, K. R., et al. Heavy metal exposure from foods. Environ. Health Perspect. 12: 63 (1975).